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Standard Recommended Practice for QUALITATIVE IDENTIFICATION OF POLYMERS IN EMULSION PAINTS¹

This Standard is issued under the fixed designation D 3168; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reappraisal.

1. Scope

1.1 This recommended practice describes a procedure for the qualitative identification in emulsion paints of most types of polymers present as major components of the paint vehicle. Limitations are discussed in Sections 4 and 10.

2. Applicable Documents

2.1 *ASTM Standards:*

- D 2621 Infrared Identification of Vehicle Solids from Solvent-Type Paints²
- E 131 Definitions of Terms and Symbols Relating to Molecular Spectroscopy³
- E 275 Recommended Practice for Describing and Measuring Performance of Spectrophotometers³

3. Summary of Method

3.1 The vehicle is extracted from the dried paint and after filtering is cast on a salt plate. The infrared spectrum is obtained and compared with reference spectra for identification of major components.

3.2 The paint is applied to a filament and pyrolyzed to depolymerize the vehicle. An internal standard is added and the pyrolyzate is separated into its components by gas-liquid chromatography. Monomers are identified by comparison of relative retention times.

4. Significance

4.1 Identification of specific acrylic polymers in emulsion paints is often difficult or impossible by infrared alone. This is particularly true when the acrylic is present in a small amount as a comonomer with vinyl acetate, or when blended with alkyds or other ester sys-

tems. If identification of an acrylic component is required in such a system, it may often be accomplished by gas chromatographic analysis of the pyrolyzed paint film. The presence of a number of other polymers may often also be confirmed by pyrolysis since they produce characteristic and reproducible pyrograms.

4.2 The pyrograms obtained from unknown samples will vary in complexity according to the sample composition. It is necessary to establish the presence or absence of as many components as possible from a study of the infrared spectral data obtained in the first part of this method. The gas chromatography data may then be used to help identify any unknown components present and to confirm identifications made by infrared.

5. Definitions

5.1 For definition of terms and symbols, refer to Method E 131.

6. Apparatus

6.1 *Spectrophotometer*, recording, double-beam, infrared, with a range from at least 2.5 μm to 15 μm and a spectral resolution of at least 0.04 μm over that range. For checking the performance of the infrared spectrophotometer, see Recommended Practice E 275.

6.2 *Cell Mount*, demountable.

6.3 *Halide Salt Crystals*, for use with demountable cell mount.

¹ This recommended practice is under the jurisdiction of ASTM Committee D-1 on Paint, Varnish, Lacquer, and Related Products.

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² 1974 *Annual Book of ASTM Standards*, Part 27.

³ 1973 *Annual Book of ASTM Standards*, Part 30.

6.4 *Oven*, gravity or forced-draft, that will maintain the temperature between 105 and 110°C.

6.5 *Linear Programmed Temperature Gas Chromatograph*, equipped with a thermal conductivity detector.

6.6 *Pyrolysis Accessory*—Any suitable apparatus for achieving pyrolysis external to the chromatograph, that results in the recovery of sufficient pyrolyzate for identification purposes. The apparatus described in the Annex has been found to meet these requirements.

6.7 *Gas Chromatographic Column*, 10 ft (3 m) in length, $\frac{1}{4}$ in. (6.4 mm) in outside diameter copper tubing packed with 10% silicone resin⁴ on 80 to 100-mesh acid-washed, dimethyl-dichlorosilane treated calcined diatomaceous earth.⁵

6.8 *Steam Bath or Low Temperature Hotplate*.

6.9 *Flask*, small Dewar.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Extraction Solvent Mixture*—Equal volumes of reagent grade *o*-dichlorobenzene, dimethylformamide, and tetrahydrofuran.

7.3 *Liquid Nitrogen*.

7.4 *Petroleum Ether* (30 to 60°C boiling range) reagent grade, or hexane, reagent grade.

8. Procedure—Infrared Analysis

8.1 Transfer 1 to 2 g of emulsion paint to a 100-ml borosilicate glass beaker. Add approximately 2 ml of distilled water and swirl or use a clean glass rod to spread the paint uniformly over the bottom of the beaker.

8.2 Place the beaker in an oven at 105 to 110°C for at least 2 h, breaking up any skins that form so that complete drying is ensured.

8.3 Add 50 ml of distilled water, cover with a watchglass, and place on a steam bath or low-temperature hotplate for 1 h. This process

removes emulsifiers, protective colloids, and other water-soluble components that might interfere with interpretation of the infrared spectrum. Decant off the clear water layer and discard. If the addition of the distilled water to the dried paint film produces a milky dispersion, the drying step in 7.2 was not complete and should be repeated.

NOTE 1—If there is an interest in characterization of the emulsifier system used, the water should be filtered through a fine-texture filter paper and taken to dryness. The solids may then be examined by infrared.

8.4 Dry for 15 to 20 min in an oven at 105 to 110°C. Add 50 ml of petroleum ether or hexane, cover with a watchglass, and bring to a slow boil for approximately 5 min. This process removes most emulsified plasticizers, oils, and other water insoluble, nonpolymeric organic materials, which might also interfere with the interpretation of the infrared spectrum. Decant off the solvent and discard.

NOTE 2—If there is an interest in characterizing the water-insoluble petroleum ether soluble fraction, it should also be filtered through fine-texture paper, taken to dryness, and examined by infrared.

8.5 Add 10 ml of the extraction solvent mixture (7.1) and place on a steam bath or low-temperature hotplate for approximately 1 h. Filter, while still hot, through a fine-texture filter paper. If the polymer solution is viscous, it may be diluted further with extraction solvent mixture and warmed prior to filtration. Alternatively, the pigment may be removed from the polymer solution by centrifuging. Evaporate the solution on the steam bath or hotplate to a volume of 1 ml or less.

8.6 Place the concentrated polymer solution on a halide salt crystal and spread to form a uniform film. The thickness of the film should be such that when the infrared spectrum is recorded, the transmittance of the strongest band falls between 5 and 15%. Dry the film in an oven at 105 to 110°C for 1 h and cool in a desiccator.

8.7 Record the infrared spectrum from 2.5 to 15 μm so that a spectral resolution of 0.04 μm is maintained throughout that range. (Methods for achieving this resolution will vary

⁴ Silicone resin SE-30 produced by General Electric Co., has been found satisfactory.

⁵ Chromosorb W produced by Johns Manville Co., has been found satisfactory.

according to the directions of the manufacturer of the instrument used.)

8.8 Compare the spectrum obtained with reference spectra prepared in a similar manner from emulsion paints of known composition or with published collections of polymer spectra such as Method D 2621. Other sources are listed in the references. (1 to 8)^a

9. Procedure—Pyrolysis-Gas Liquid Chromatography

9.1 Coat the resistance wire filament of the pyrolysis unit by dipping it into the original paint sample to be tested. Remove the volatiles either by drying the filament in an oven for about 30 min at 105°C or by heating it electrically with the power supply set at 1 or 2 A [100 to 200°C] for approximately 10 min. If a larger volume of pyrolyzate is required than would be produced by the initial amount of sample deposited, additional layers of coating may be added by repeating the dipping and drying steps.

9.2 Place the coated filament-vial cap assembly in a small beaker. Extract with water, followed by petroleum ether or hexane, as outlined in 8.3 and 8.4.

9.3 Add a few drops of liquid nitrogen to the vial or flush with nitrogen gas to prevent oxidation reactions from occurring during the pyrolysis.

NOTE 3—If the infrared spectrum obtained in Section 8 shows poly(vinyl acetate) or poly(vinyl chloride) to be present, the pyrolysis step should be modified to prevent the acetic or hydrochloric acid formed from degrading other monomers which may be present in the pyrolyzate. Addition of a drop of concentrated ammonium hydroxide to the vial just prior to pyrolysis, neutralizes the acid as it is formed. The pyrolyzate may then be recovered by solubilization in diethyl ether just before sampling.

9.4 Tightly screw the coated filament-cap assembly onto the glass vial and connect the filament leads to the power supply.

9.5 Submerge the entire vial in liquid nitrogen contained in a small Dewar flask. Allow to equilibrate for several minutes, then apply a predetermined current for approximately 10 to 15 min.

NOTE 4—The optimum temperature which varies for different polymer types may be determined experimentally from known polymer systems. Six amperes (approximately 600°C) has been found to be close to optimum for the types tested. A study of the pyrolysis of acrylic polymers showed that heating

times varying from 10 to 30 min produced no significant differences in the composition of the pyrolyzate.

9.6 Turn off the power supply and allow the filament to cool for several minutes. Remove the vial from the liquid nitrogen and substitute a standard screw cap for the filament-cap.

9.7 Using a syringe, add *n*-butyl acetate to the pyrolyzate equal to approximately 20% of the pyrolyzate volume.

9.8 Install the silicone resin column in the chromatograph and allow to condition to 200°C. Set up the following conditions on the chromatograph:

Detector cell temperature, °C	270
Detector cell current, mA	150
Injection port temperature, °C	270
Carrier gas	helium
Flow at exit, ml/min	60
Starting column temperature, °C	70
Finishing column temperature, °C	200
Column heating rate, °C/min	6

9.9 Inject 5 μ l of pyrolyzate into the chromatograph, engage the chart drive and start the temperature programmer. Attenuate as necessary during the run.

9.10 Calculate retention time data relative to the *n*-butyl acetate internal standard peak for each major peak obtained. Compare relative retention times obtained with known values for monomers of interest (see 8.8).

NOTE 5—The use of the method described will minimize the tendency of pyrolysis products to undergo secondary reactions while still in the vapor state. This simplifies the chromatograms obtained, making interpretation easier.

9.11 If any doubt remains concerning an identification based on the pyrogram obtained, it is strongly recommended that the peak of interest be trapped as it is eluted from the chromatograph for subsequent positive identification by infrared spectroscopy or mass spectrometry.

9.12 Burn off any remaining organic residue by applying 8 or 9 A for a few seconds. Disconnect the filament from the power supply; then clean off any adhering pigment by gently brushing with a test tube brush while holding the filament under running water. The same filament may be reused many times.

^a The boldface number in parenthesis refer to the list of references at the end of this recommended practice.

10. Interferences

10.1 Dibutyl maleate and dibutyl fumarate monomers are not successfully recovered by this procedure. If their presence is suspected as comonomer in a vinyl acetate copolymer system, *n*-butyl alcohol should be found in the pyrolyzate. This evidence, together with the absence of butyl acrylate or butyl methacrylate monomer peaks, is an indirect indication of the presence of one or both of these monomers.

10.2 The presence of relatively low quantities of copolymerized acids may not be successfully established by this procedure, due to

some unavoidable decomposition of acrylate and methacrylate esters to acrylic or methacrylic acid and the corresponding alcohols during the pyrolysis. The infrared spectrum and an acid number determination, both run on the polymer solids, may usually be relied upon to establish the presence or absence of acid groups in the polymer.

10.3 In the case where the polymer being analyzed is simple (such as a vinyl acetate-alkyl ester copolymer, or a single acrylate - methacrylate copolymer), it might be advantageous to examine the total pyrolyzate directly by infrared (as a solution in carbon disulfide).

REFERENCES

- (1) Chicago Society for Paint Technology, Infrared Spectroscopy Committee, *Infrared Spectroscopy, It's Use in the Coatings Industry*, Federation of Societies for Paint Technology, Philadelphia, Pa., 1969.
- (2) Sadtler Commercial Infrared Spectra, Sadtler Research Laboratories, Inc., Philadelphia, Pa.
- (3) Nyquist, R. A., *Infrared Spectra of Plastics and Resins*, 2nd Ed., Dow Chemical Co., Midland, Mich., May 1961.
- (4) Haslam, J., and Willis, H. A., *Identification and Analysis of Plastics*, D. Van Nostrand Co., Inc., New York, N.Y., 1965.
- (5) Weinberger, L. A. and Kagarise, R. E., "Infrared Spectra of Plastics and Resins," *OTS Bulletin* No. PB-111438, U. S. Dept. of Commerce, May 1954.
- (6) Clark, G. L., Ed., *The Encyclopedia of Spectroscopy*, Reinhold Publishing Corp., New York, N. Y., 1960, p. 506-15.
- (7) Hummel, D. O., *Infrared Analysis of Polymers, Resins, and Additives. An Atlas Vol 1 Plastics, Elastomers, Fibers, and Resins*, Wiley Interscience, New York, N. Y. 1969

TABLE 1 Relative Retention Times^a

Monomer or Alcohol	Relative Retention
Methanol	0.13
Ethanol	0.16
Acrylonitrile	0.25
Vinyl acetate	0.37
Methyl acrylate	0.45
Isobutanol	0.48
<i>n</i> -Butanol	0.57
Ethyl acrylate	0.66
Methyl methacrylate	0.72
Ethyl methacrylate	0.93
<i>n</i> -Butyl acetate	1.00
Isobutyl acrylate	1.15
<i>n</i> -Butyl acrylate	1.29
Styrene	1.33
Hydroxyethyl acrylate	1.38
Isobutyl methacrylate	1.43
Butyl methacrylate	1.55
Vinyl toluene	1.64
2-Hydroxyethyl methacrylate	1.64
2-Ethylhexanol	1.72
2-Ethylhexyl acrylate	2.31
2-Ethylhexyl methacrylate	2.56

^a Relative retention times listed are meant to serve as a guide for identification purposes. It should be understood, however, that the numbers listed are not absolute, and will vary somewhat from laboratory to laboratory and from instrument to instrument. For maximum accuracy in making identifications from retention time data, each analyst should prepare his own table by running the monomers of interest under the same conditions used for the analysis of the pyrolyzate.

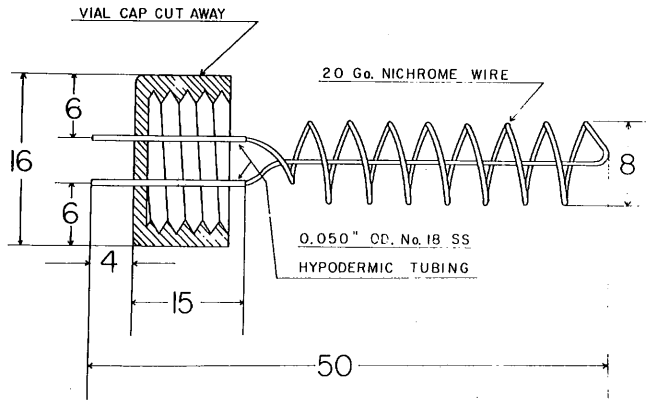
ANNEX

A1.1 PYROLYSIS ACCESSORY

A1.1 A 320 mm (12.5 in.) of 20 gage Nichrome wire is wound in a helix configuration as shown in Fig. A1. The characteristics of the filament have been chosen so that the current in amperes $\times 100$ closely approximates the temperature of the filament in degrees Celsius. Two 15-mm (0.6-in.) lengths of 1.3 mm (0.05 in.) outside diameter. Number 18 stainless steel hypodermic tubing is crimped onto the filament

ends and inserted through snugly fitting holes which have been drilled through the cap of a 15 by 45-mm (1-dram) vial (see drawing for detail). The hypodermic tubing, which functions as a heat sink to prevent pyrolysis of the plastic cap, may be firmly fastened to the cap by means of an epoxy cement.

A1.2 The tubing ends are connected by means of alligator clips to the leads of a suitable power supply.



ALL DIMENSIONS IN MILLIMETERS UNLESS NOTED

FIG. A1 Pyrolysis Accessory.

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